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Behaviour of limecrete under fire conditions

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SUMMARY

Hydraulic lime concrete (limecrete) is a material that has a lower environmental impact than that of ordinary Portland cement (OPC) concrete and, consequently, may be increasingly used in some construction applications. Because of its reduced strength, pozzolanic materials, such as metakaolin, are commonly used to improve its strength and durability. Simultaneously, to the increased interest in more sustainable materials, the fire behaviour of materials has also deserved an increased attention during the last years because of some important disasters that occurred.

In this study, the fire behaviour of limecrete has been investigated. To increase limecrete performance, hydraulic lime has been replaced by metakaolin in different percentages. Fire tests at different temperatures (200, 400, 600 and 830°C) and different durations (30 and 60 min) have been performed and the residual strength and chemical changes using X-ray powder diffraction and thermogravimetric analysis techniques were investigated. It became apparent that a 20% replacement of hydraulic lime by metakaolin leads to an improved performance at room temperature and fire loading. Copyright © 2011 John Wiley & Sons, Ltd.

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1. INTRODUCTION

The effects of fire on Portland cement concrete are well known, and studies have been conducted in order to evaluate variations in chemical and mechanical characteristics of concrete with varied pozzolanic additions, under the effect of fire. Factors that affect the degradation of concrete are the heating and cooling rates, that is the peak temperatures that lead to phase transformations and differential thermal expansion of constituent materials.

There is very little information regarding the behaviour of hydraulic lime concrete under fire conditions. Regarding the effect of temperature on the compressive strength of Portland cement concrete, there is more information, but nevertheless, there are still several unknown issues and questions. An important issue related to the fire behaviour of concrete is that, in fact, this behaviour is dependent on a variety of factors such as, for example, type of binder, aggregate, water–cement ratio, testing conditions (load–heat sequence, loading, boundary conditions) or curing conditions [1–8].

The increase of temperature produces transformations in the paste and in the aggregates. In the cement paste, the following reactions occur: release of chemically bound water (100–200°C), dehydration of calcium silicate hydrate (CSH) around 300°C, dissociation of $Ca(OH)_2$ at 490°C, and further decomposition of CSH at 600°C. In terms of transformations of the aggregate, the following

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changes occur: thermal expansion of calcareous aggregates at 300°C, phase transformation of quartz at 570°C, decarbonation of calcareous aggregates between 600°C and 900°C, and melting of feldspars at 1150°C [6,9,10].

Results of concrete incorporating pozzolanic materials suggest a better performance at lower temperatures (up to 300°C) but higher degradations at superior heating temperatures [4]. This may be due to an increase in spalling caused by a densification of the concrete structure by the addition of pozzolans.

The pozzolanic material used for this study was metakaolin as it is an emergent material for use in concrete in Portugal and should be used at a large scale in a few years, substituting current pozzolanic materials such as fly ash. As an attempt to promote concrete that is more ecological, Portland cement was replaced by hydraulic lime (NHL5) that, however, has more restrictions in terms of applicability. This change in the main binder has almost no influence on chemical changes with temperature as the basic constituents are the same but with a different ratio.

Available results that show the influence of temperature on the compressive strength of concrete exhibit large scatter [5,11]. Generally speaking, concrete residual strength decreases with increasing temperature [2,5,6] being normally considered that beyond 500°C, concrete looses almost all its structural aptitude. These factors are included in structural concrete design codes such as Eurocode [12]. The effect of loading during heating generally improves the strength when compared with unloaded specimens because it seems that compression reduces crack formation [5,13]. The cooling rate also seemed to influence the residual strength of concrete as presented in [2]. It shows that for temperatures above 600°C, the cooling rate is not relevant, but for lower temperatures, fastest cooling rates lead to lower residual strength. Unsealed conditions, which allow moisture to freely escape from concrete, also seemed to improve the residual strength compared with sealed conditions [11,13].

This study, based on an experimental campaign, has the aim of evaluating the behaviour of limecrete (hydraulic lime concrete) under fire conditions, as well as the impact of the addition of pozzolans. To achieve this goal, limecrete was studied before and after fire exposure by assessing the variation in mechanical resistance, namely compressive strength, as well as chemical and physical changes.

2. MATERIALS

Binders were characterized in terms of their chemical and mineralogical composition, using X-ray fluorescence (Philips PW 1400 X-ray fluorescence spectrometer, Philips, Amsterdam, The Netherlands) and X-ray diffraction (Philips X'Pert Pro X-ray diffractometer). Aggregates were characterized in terms of their particle size distribution following standard EN 12620:2002, Aggregates for concrete.

Natural hydraulic lime, produced in Portugal, was used as the main binder. Strength development of NHL5 amounts to 5 MPa at the age of 28 days, but this value may be improved by the addition of pozzolanic materials. Chemical composition of Portuguese NHL5 is shown in Table I. In terms of crystalline phases, this hydraulic lime is mainly composed of portlandite, dicalcium and tricalcium

Table I. Chemical composition of metakaolin and hydraulic lime (percentage in weight).

Oxides	NHL5	MK
CaO	43.13	0.04
SiO_2	22.45	59.90
Al_2O_3	7.07	32.29
Fe_2O_3	2.82	1.28
K_2O	1.67	2.83
MgO	2.13	0.17
Na_2O	0.59	0.24
TiO_2	0.38	0.36
Na_2O	0.59	2.83
LOI	18.60	2.80

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silicates, showing a high burning temperature. The presence of calcite is due to some carbonation that has taken place whilst the presence of quartz is also identified.

Metakaolin was obtained by the calcination of kaolinitic clays over a specific temperature range and was finely ground, ensuring a high specific surface that enhances pozzolanic reactivity. The Chapelle test [14] was used to measure the amount of $Ca(OH)_2$ that is used in the pozzolanic reaction. The application of the Chapelle test to metakaolin showed a pozzolanic reaction with the consumption of 0.394 g of $Ca(OH)_2$ per gram of metakaolin. X-ray powder diffraction (XRD) results revealed the presence of quartz and kaolinitic minerals whilst in terms of chemical composition; in Table I, a predominance of silica and alumina is shown.

River sand of siliceous composition and calcareous coarse aggregate (CA) were used for this study. The sand particle size distribution is in the range of 0–4 mm. CAs have a particle size distribution in the range of 5–25 mm.

Concrete mixes are shown in Table II and comprise a basic mix with no metakaolin (M0) and two other mixes in which there is a substitution, in weight, of hydraulic lime by a Portuguese metakaolin. Mixture M2 has 20% replacement, and mixture M3 has 30% of cement substitution. The water content was kept constant with a water/binder ratio of 0.5. Concrete was moulded on $100 \times 100 \times 100\,mm^3$ cubes.

Concrete was cured in a climatic chamber with 95% relative humidity at a temperature of 20°C for 28 days. After that, the specimens were kept in a climatic chamber with 60% relative humidity at a temperature of 20°C until the day of testing.

3. METHODS

3.1. Testing under fire conditions

Fire testing of the concrete was performed using a standard vertical furnace. The furnace measures $3.1 \times 3.1 \times 1.2\,m^3$ and can reach temperature of 1200°C. The temperature and the pressure inside the furnace were monitored during the tests. The pressure imposed within the furnace was kept constant at −0.42 Pa at the zone where the specimens were located; during the tests, small deviations to this value were recorded, but always inside of the permitted deviations allowed in the standard EN 1363-1 [15]. Five different fire tests were performed with the maximum temperature ranging from 200°C to 843°C (see Table III and Figure 1 where T12, T13 and T14 are the furnace thermocouples readings). The test duration was 30 min except for the case where the maximum temperature was 400°C where an additional test of 60 min was performed. The temperature increase follows the ISO 834 fire curve [16] given by Equation (1):

$$T = 20 + 345 \log(8t + 1) \tag{1}$$

in which T is the temperature in °C and t is the time in minutes. After the maximum temperature is attained, it is kept constant until the end of the test. Concrete cubes were kept unloaded during the fire test.

The aim of the used fire testing procedure was to evaluate the post-fire resistance of limecrete after different fire exposures. Because the ISO-fire is the most widely accepted and used in experimental fire tests, it was used as the heating curve. The temperature distribution inside the tested specimens was not uniform, but this is what happened in a real fire situation.

Table II. Mixture composition including hydraulic lime percentage in the binder (p).

Constituents	Series name		
[kg/m^3]	M0	M2	M3
CA	1074	1074	1074
Sand	321	321	321
NHL5	550	440	385
MK	–	110	165
Water	247.5	247.5	247.5

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Table III. Fire tests.

	Maximum temperature	Test duration	Time to reach maximum temperatures
	[°C]	[s]	[s]
F230	200	1800	20
F430	400	1800	90
F630	600	1800	360
F830	843	1800	1800
F460	400	3600	90

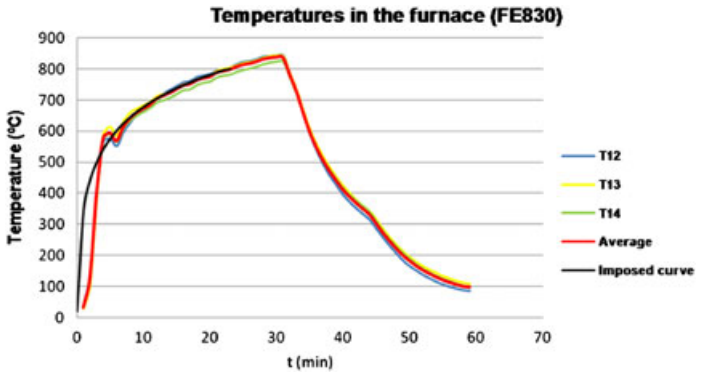

Figure 1. Temperature–time curves in furnace thermocouples during the test FE830.

3.2. *Compressive tests*

The compressive tests on concrete were used to assess concrete strength before and after fire tests. Tests were performed on $100 \times 100 \times 100\,mm^3$ specimens. For each limecrete series, 39 cubes were made: three cubes were tested at 28 days, three were tested at 90 days, three specimens were tested at the day of the fire test to assess the pre-fire compressive strength, and the remainders were tested in fire (six cubes for each temperature–duration test). Testing procedure follows that of the Portuguese version of the European standard NP EN 12390-3:2003 [17].

After the fire test, the specimens were cooled naturally and tested in compression. Because of spalling that occurred in some specimens, the two best cube faces were used for the base and top of the specimen during the test, and the compressive strength was evaluated by dividing the ultimate force by the area of the cube face (100×100 m^2), thus giving a nominal strength.

3.3. *Chemical analysis*

Changes in mechanical behaviour are related to the physical and chemical transformations that occurred during the heating process. In order to obtain a complete characterization of the obtained samples, after firing, mineralogical, thermal, chemical, and mechanical analyses were performed. The adopted methodology was considered in order to understand the degradation model of concrete with the effect of metakaolin incorporation, under fire conditions.

X-ray powder diffraction enables the identification of crystalline phases present. The amorphous components, such as soluble silicates from hydraulic reactions, are very difficult to detect or are even not identifiable. The XRD analysis were performed with a Philips X'Pert PW 3040/60 goniometer, using CuKα radiation, with operational conditions of 30 mA and 50 kV, automatic divergent notch graphite monochromator and a step size of 1°/2θ/min in the 4°–65° 2θ range, with data acquisition using Philips X'Perta Data Collector v1.2, after the samples were dried at 60°C, grounded and pulverized in an agate mortar. Identification of crystalline phases by XRD was carried out using the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

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Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) allow for the identification and quantification of concrete compounds, detecting the presence of products from hydraulic reactions. The TGA and DSC were carried out simultaneously in powder samples dried, at room temperature, in a desiccator, using a Netzsch Júpiter STA 449 (Netzsch, Selb, Germany) balance. The heating rate was 10°C/min., up to 1100°C. The sample preparation also followed the procedure used for XRD analysis.

4. RESULTS AND DISCUSSION

4.1. Compressive strength

The results of compression tests clearly indicate that metakaolin has a very positive effect on the strength of limecrete. Comparing with 28 days strength of standard limecrete at least 50% increase can be observed for mixture M3, and in the case of mixture M2, it is as high as 66% (see Figure 2). At the age of 90 days, approximately the same percentage of strength increases can be observed. This behaviour agrees with previous results [18,19]. When the strength at 90 days is compared with 28 days strength for each mixture, strength increases of 17%, 40% and 30% for mixtures M0, M2 and M3, respectively, can be observed. This seems to indicate that limecrete with metakaolin reveals a slower strength development than standard limecrete.

After cooling, the specimens were tested in uniaxial compression and the residual strength compared with the room temperature strength. Figure 3 represents the relative residual strength for the different series at different temperatures. The relative residual strength is defined as the ratio at the age of fire testing between compressive strength of specimens not tested under fire conditions and those submitted to fire loading. The shaded blue area represents the residual compressive strength according to CEB Bulletin 208 [2], resulting from concrete submitted to different temperatures and to a quick cooling process.

The M2 series, with 20% metakaolin, had a better overall performance. From these results the limecrete concrete with metakaolin had a higher relative residual strength than Portland cement concrete for all the temperatures (see Figure 3), with residual strength of about 45% for 800°C.

In Figure 4, the relative residual strength for each series is presented. As expected, there is a considerable reduction of strength at high temperatures. The M0 series has a residual strength of 60% for 600°C followed by a sharp reduction to 30% at 830°c. As for the M2 series, the reduction is more gradual, starting at 630°C. The M3 series had a considerable drop of strength at 630°C. As for the exposure time, there was no significant difference between the 30-min test, F430, and the 60-min test, F460.

4.2. Concrete surface

One of the aims of this research was to study the change in the surface texture and colour with temperature. With these results, it is possible to estimate to what temperature concrete had been

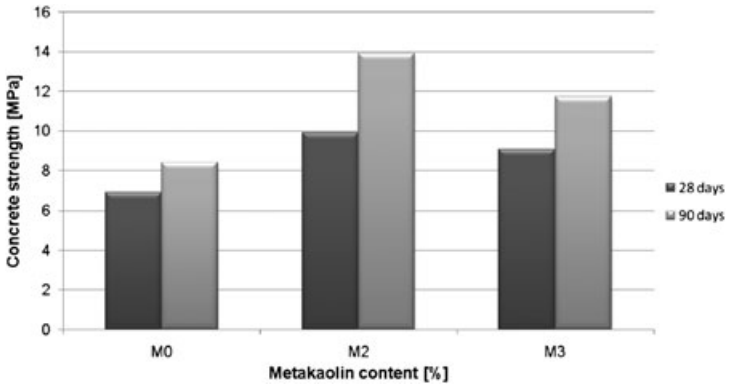

Figure 2. Compressive strength of the three mixes at 28 and 90 days.

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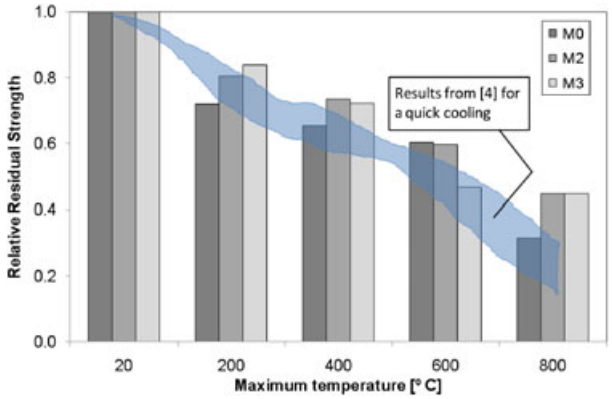

Figure 3. Relative residual strength for the different series at different temperatures.

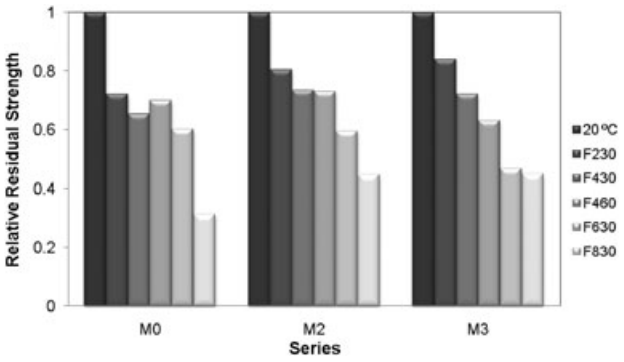

Figure 4. Relative residual strength for each series.

exposed during a real fire. Figure 5 shows photographs of representative specimens of the three series at different temperatures. There were no considerable differences in the behaviour of the three different series. At 200°C, there are no significant changes in the surface. At 400°C, concrete starts spalling; at this temperature, spalling is superficial and limited to a small percentage of the surface. For 400°C, there is a much higher spalling; most of the surface mortar spalls. At 600°C, small fragments of concrete including the CA start splitting. At 800°C, larger fragments spall off, and in some of the specimens, cracking was observed.

Surface colour change is noticeable at 600°C, and at this temperature, the concrete's surface turned from grey to pink.

4.3. Chemical analysis

Hydraulic lime hardens by hydration of C_2S forming CSH and carbonation forming $CaCO_3$. Cement hardens mainly by hydration of C_3S and some C_2S forming CSH. Carbonation reaction is residual in cement-based concrete. The main products of metakaolin reaction with cement or hydraulic lime are CSH and gehlenite. Decomposition of CSH with heat (100°C–800°C) produces C_2S and CS and C_2S tends to re-hydrate with humidity. Decarbonation in hydraulic lime-based concrete will occur in the interval of 700°C–900°C.

4.3.1. Material characterization. The XRD patterns after thermal transformations, Figure 6, are similar with and without metakaolin at all temperatures. They are mainly composed by quartz (ICDD PDF 33-1161) and calcite (ICDD PDF 5-586) and minor amounts of k-feldspar (ICDD PDF 22-687), muscovite (ICDD PDF 7-25) and gehlenite (ICCDD PDF 9-216). The slight difference in each diffractogram for all groups is the apparent increase of gehlenite with temperature, facilitated by the evidence of this phase at 20°C, which means that it is already nucleated. This fact may play an

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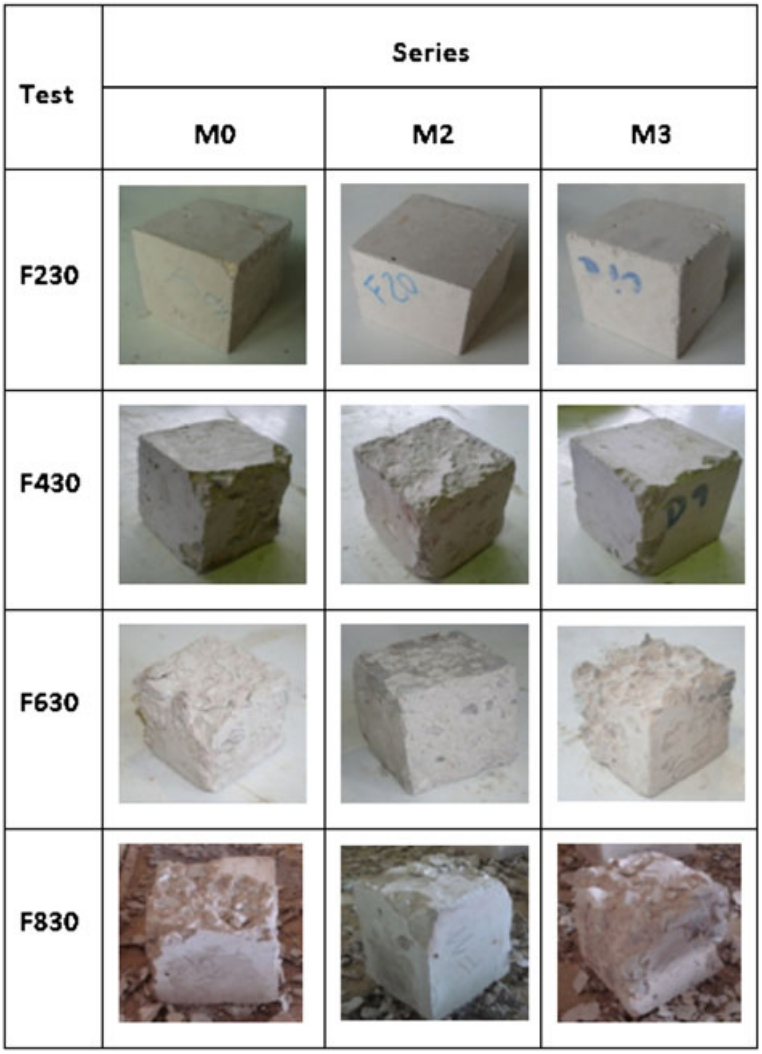

Figure 5. Concrete surface exposed to high temperatures.

important role in the fire behaviour of hydraulic lime concrete with metakaolin as there seems to be no degradation of gehlenite with temperatures up to 800°C.

4.3.2. Thermal behaviour. The thermal behaviour, for all samples (as the example shown in Figure 7 for mixtures M0 and M3 at 800°C), has the same pattern. In the TGA, the only evident reaction is the decarbonation (decomposition of calcite into lime and carbon dioxide) between 750°C and 820°C, which is less significant, as expected, with the addition of metakaolin. In DSC, the first endothermic reaction is visible from the beginning until 150°C related with water de-adsorption and CSH dehydration [9,20]; therefore, no other dehydration reactions related with CS phases are evident in any thermogram analyzed. A slightly endothermic reaction at near 573°C related with the allotropic transformation of quartz α in quartz β and the most evident endothermic reaction of the decarbonation at the same thermal interval as in the TGA thermogram and in corroboration with the XRD pattern. This means that, even at 800°C, the decarbonation effect by the fire was very low, which indicates that the principal degradation effect in the samples is physical, that is by spalling. Handoo *et al*. [21] stated that, for OPC concrete, when the temperature reaches beyond 500°C in a structural element, the damage is quite rapid, and a detailed survey should be carried out to determine its structural integrity. Hydraulic lime concrete should behave in a similar way because of the similarity to OPC regarding hydration products. However, with the addition of metakaolin, this behaviour may be improved because of the stability of gehlenite when exposed to high temperatures.

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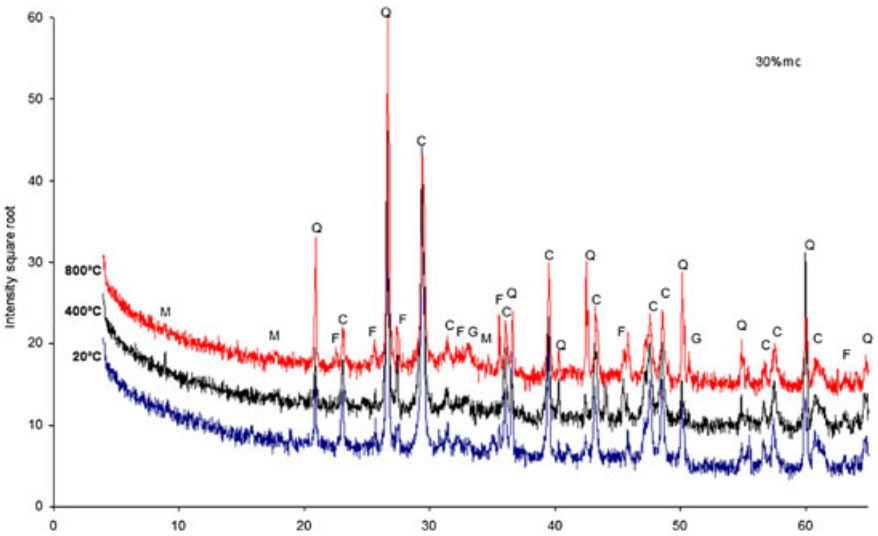

Figure 6. X-ray powder diffraction pattern of the samples group with addition of 30% of metakaolin. Q, quartz; C, calcite; F, K-Feldspars; G, Gehlenite.

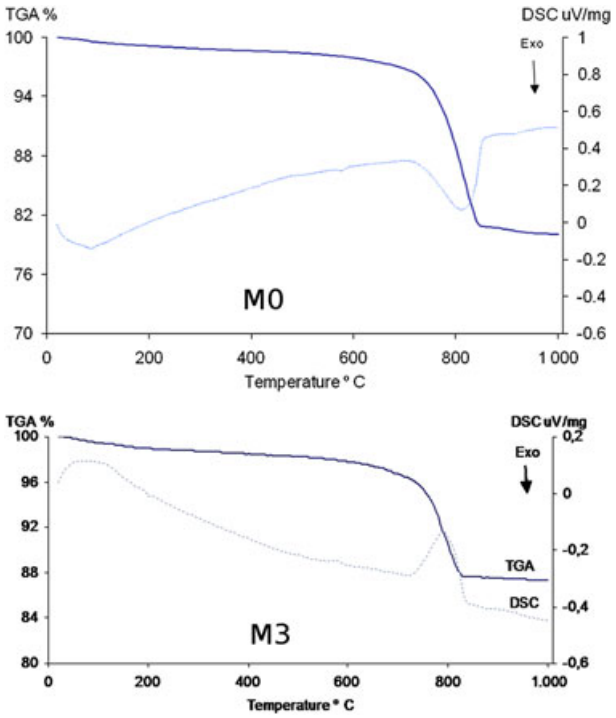

Figure 7. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of samples with addition of reference mixture and with 30% of metakaolin fired at 800°C.

5. CONCLUSIONS

Limecrete is a material with some application in the construction sector and with the advantage of lower environmental impact when compared with OPC concrete. The addition of pozzolanic material allows for an increase in mechanical strength and a possible increment in terms of concrete durability. It is in this field, taking into account the behaviour of this material under fire conditions, that this research was undertaken. It became clear that a substitution of 20% of hydraulic lime by metakaolin was advantageous both in terms of mechanical behaviour at room temperature and also in terms of

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residual mechanical strength after fire exposure, possibly because of the formation of gehlenite. No significant chemical changes were observed using XRD and TGA techniques, suggesting that loss of mechanical strength after fire exposure is induced by physical effects.

REFERENCES

1. Kodur VKR, Phan L. Critical factors governing the fire performance of high strength concrete systems. *Fire Safety Journal* 2007; **42**(6–7):482–488.
2. CEB. *Fire Design of Concrete Structures (in accordance with CEB/FIP Model Code 90)*. Bulletin 208. FIB: Lausanne, Switzerland, 1991.
3. Xu Y, *et al*. Impact of high temperature on PFA concrete. *Cement and Concrete Research* 2001; **31**(7):1065–1073.
4. Savva A, *et al*. Influence of elevated temperatures on the mechanical properties of blended cement concretes prepared with limestone and siliceous aggregates. *Cement and Concrete Composites* 2005; **27**(2):239–248.
5. FIB. *Fire Design of Concrete Structures—Materials, Structures and Modelling—State of the Art Report*. Bulletin 38. FIB: Lausanne, Switzerland, 2007.
6. FIB. Fire Design of Concrete Structures—Structural Behaviour and Assessment—State of the Art Report. Bulletin 46. FIB: Lausanne, Switzerland, 2008.
7. Demirel B, Kelestemur O. Effect of elevated temperature on the mechanical properties of concrete produced with finely ground pumice and silica fume. *Fire Safety Journal* 2010; **45**(6–8):385–391.
8. Ismail M, *et al*. Influence of elevated temperatures on physical and compressive strength properties of concrete containing palm oil fuel ash. *Construction and Building Materials* 2010; in press, Corrected Proof.
9. Arioz O. Effects of elevated temperatures on properties of concrete. *Fire Safety Journal* 2007; **42**(8):516–522.
10. Gonçalves MJCR. Comportamento ao fogo de elementos estruturais de betão análise numérica e metodologia. Faculty of Engineering, Porto, University of Porto. PhD: 790, 2008.
11. Nanstad R. A review of concrete properties for prestressed concrete pressure vessels, Oak Ridge National Laboratory. ORNL/TM-5496—October 1976.
12. CEN. EN 1992-1-2:2004. *Eurocode 2: Design of Concrete Structures—Part 1–2: General Rules—Structural Fire Design*. CEN: Brussels, Belgium, 2004.
13. Lankard DR, *et al*. *Effects of Moisture on the Structural Properties of Portland Cement Exposed to Temperatures up to 500°F*. ACI: Detroit, 1971.
14. AFNOR. NF P 18-513. *Métakaolin, Addition Pouzzolanique pour Bétons—Définitions, Spécifications, Critères de Conformité*. AFNOR: Saint Denis, France, 2010.
15. CEN. EN 1363-1. *Fire Resistance Tests. Part 1—General Requirements*. CEN: Brussels, Belgium, 1999.
16. ISO. ISO 834. *Fire-resistance Tests—Elements of Building Construction*. ISO: Brussels, Belgium, 1975.
17. IPQ. NP EN 12390-3:2003. *Ensaios do Betão Endurecido. Parte 3: Resistência à Compressão dos Provetes de Ensaio*. IPQ: Lisbon, Portugal, 2003.
18. Velosa AL, Cachim PB. Hydraulic-lime based concrete: strength development using a pozzolanic addition and different curing conditions. *Construction and Building Materials* 2009; **23**(5):2107–2111.
19. Cachim P, *et al*. Effect of portuguese metakaolin on hydraulic lime concrete using different curing conditions. *Construction and Building Materials* 2010; **24**(1):71–78.
20. Harmathy TZ. Thermal properties of concrete at elevated temperatures. *ASTM Journal of Materials* 1970; **1**(5):47–74.
21. Handoo SK, *et al*. Physicochemical, mineralogical, and morphological characteristics of concrete exposed to elevated temperatures. *Cement and Concrete Research* 2002; **32**(7):1009–1018.

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